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Broadening of the resonance Cu I lines in the laser-induced copper spectrum



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ARTICLE INFO

Article history: Received 17 April 2013 Received in revised form 18 September 2013 Accepted 19 September 2013 Available online 7 October 2013

Keywords: LIBS Emission spectroscopy Line broadening Stark effect

1. Introduction

Copper (Cu) is one of the most exploited elements in the various fields of the industry and technology [1–3]. It has two stable isotopes: ⁶³Cu and ⁶⁵Cu (69.2% and 30.8% abundances, respectively) with isospins of 3/2. The spectral line characteristics of the copper atoms (Cu I) are affected by both the isotope shift (IS) and hyperfine structure (HFS) due to considerable isospin. The intense resonance 324.754 nm and 327.396 nm lines are good candidates for diagnostic purposes in various applications. Due to different kind of broadenings one can expect a complex profile of Cu I lines, especially the resonance 324.751 nm and 327.396 nm lines. It is of interest to study the shape of these lines in realistic plasma conditions with emphasize on possible application in plasma diagnostics. Broadening mechanisms for certain number of the visible range Cu I spectral lines have been investigated in laser-generated plasma by Song et al. [4] and Man et al. [5]. In the plasmas with electron density (*N*) higher than 10^{22} m^{-3} and electron temperature (T) below 20 000 K the Stark broadenings are dominant broadening mechanisms in the spectral line

ABSTRACT

Broadening of the resonance 324.754 nm and 327.396 nm copper (Cu I) lines have been investigated in the laser-induced copper spectrum in the residual atmospheric pressure of 8 Pa at 19 300 K electron temperature, and electron density of 2.1×10^{23} m⁻³. The second harmonic of the Nd:YAG laser at 532 nm was applied for evaporation of atoms from the copper target. The Stark and Doppler broadening were found as the most significant mechanisms in the line shape formation at the actual plasma parameters. Measured Stark widths (*W*) were compared to existing experimental and theoretical *W* data. The role of the hyperfine structure (HFS) components in the resonance Cu I line shapes formation was, for the first time, discussed taking also into account the isotope shift (IS).

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shape formation [6]. However, the other mechanism found to be non-negligible is a Doppler broadening. The literature devoted to the Cu I resonance spectral lines Stark widths is presented in [7] and references therein. Only one experiment [8] deals with 324.754 nm Cu I line Stark FWHM (Full Width at Half Maximum, *W*). The Stark effect of resonance Cu I lines is considered theoretically in [9–11]. To the knowledge of the authors, the contribution of the hyperfine structure components on the resulting shape of the two Cu I resonance lines is discussed in only one paper [12].

The aim of this work is to present experimental Stark FWHM of the two intense resonance Cu I lines observed in the laser-induced copper plasma in the residual atmospheric pressure. We present, also, the synthetic (computed) profiles of these lines, constructed on the basis of the components in the hyperfine-structure in both of the isotopes, taking into account the isotope shift between ⁶³Cu and ⁶⁵Cu for various electron densities. The existing theoretical *W* values [9–11] were used as input parameters for a superposition procedure.

2. Experimental details

The schematic of the used experimental setup is given in Fig. 1. It is a realization of common arrangement used for single pulse laser-induced breakdown spectroscopy

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Fig. 1. The schematic of the experimental setup.

(LIBS). Copper sample (99.9% purity) was placed inside of a closed chamber in order to have controlled atmospheric pressure of 8 Pa attained by means of a mechanical pump. The chamber is mounted on an x-y translation stage which provides motion in small steps so that a fresh target surface is exposed to each consecutive laser shot. The stage itself could also be translated in the z (axial) direction for the purpose of spatially resolved measurements. The surface of the copper target was carefully polished until it was perfectly glossy. A lens of the 100 mm focal length, used for target ablation, was positioned slightly out of focus in order to create the laser spot of $\sim 0.6 \text{ mm}$ in diameter on the copper surface. The Nd:YAG laser, EKSPLA NL 311, operating at 532 nm (second harmonic) was used as a light source. Laser pulse width was 5 ns, with repetition rate of 1 Hz, delivering 6 mJ of output energy. A McPherson 209 spectrograph (Czerny–Turner geometry, 1.33 m focal length, reciprocal linear dispersion of 0.28 nm/mm in the first order) equipped with a holographic grating with 2400 grooves/mm was used. An Andor DH740-18F-03 iStar intensified CCD camera was employed as a detection system and cooled down to -20 °C for the purpose of thermal noise reduction. The instrumental profile of the spectrograph itself, in the first order measured with a 9789 QB EMI photomultiplier, corresponds to the Gaussian function with a FWHM not higher than 2.8 pm in the UV region, while the overall profile (spectrograph + ICCD camera) can be approximated by the Voigt function with a FWHM of 8.7 pm at 265 nm. The system was calibrated using a set of pen-light sources (Ne, Ar and Hg) produced by LOT-Oriel. A relative radiometric calibration of the spectrograph + ICCD camera system was carried out using a deuterium light source (StellarNet SL3-CAL) for the UV region from 200 to 400 nm and a tungsten NIST F-000 lamp for the visible range. The spectroscopic observations were made side-on (at right

angle to the laser beam direction) with a 40 mm diameter quartz lens (1:1 imaging system), used to collect and project plasma image onto a 20 μ m wide entrance slit. The recorded Cu I line image is presented in Fig. 2. In order to reduce noise the spectra were acquired by averaging 100 consecutive shots.

The detector gate width of 10 ns and appropriate gain were determined experimentally. Furthermore, a series of spatial and time-resolved measurements were also carried out to optimize parameters in terms of best signal-to-noise ratio and low continuum level. A careful analysis was conducted to determine optimal recording parameters and density decay rate, having in mind the possible departures from the LTE distributions in the case of plasma inhomogeneities, temporal variations and self-absorption, as pointed out in [13]. The recorded resonance Cu I line profiles are presented in Fig. 3.

The laser-induced plasma is essentially non-homogenous and strongly subjected to temporal variations and ambient conditions [14]. Electron density (*N*) and electron temperature (T) have values gradually changed along the radial coordinate *r* (distance from the axis defined by the laser beam) and axial position *z*, as well. The spectrum, recorded in the image mode of the ICCD camera, provides necessary data to calculate shape of the spectral line at different radial positions. This procedure is based on the inverse Abel transform. While the Abel transform itself is well defined mathematical method, its application to the real-world (noisy) data is known as numerically difficult problem. To accomplish this task number of algorithms were proposed in specialized literature [15-18]. As a background for our numerical procedure we have adopted approach proposed by Ignjatović and Mihajlov [18]. It is an elegant technique adequate for plasmas with undetermined radius, the typical case of laser-induced plasma. Relying on the Abel inverse we found that our plasma at $z \approx 2 \text{ mm}$ from the target surface emits spectrum, recorded 120 ns after the laser pulse (see Fig. 4), free of self-absorption. Namely, at the specified moment and recording position the intensity ratio of the two commonly investigated Cu I resonance spectral lines was in agreement with theoretical one, confirming absence of self-absorption



Fig. 2. The image of the 324.754 nm Cu I spectral line recorded as a result of averaging 100 consecutive shots.

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